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Example 1

Pretreatment of Porous Support

See (Step 102), FIG. 2a

5.0 g mesoporous silica (surface area: $\sim 585 \text{ m}^2/\text{g}$; pore size: $\sim 60 \text{ \AA}$; pore volume: 2.45 cc/g) as a support material was suspended in 150 mL of toluene. 1.0 mL of 3-(diethylenetriamine)propyltrimethoxysilane ("DETA silane"), was added to the suspension, representing $\sim 25\%$ of the amount of silane needed to produce a full monolayer of coverage in the support material. The mixture was stirred and heated to a reflux temperature of 110° C . Reflux was maintained for 2 hours to pretreat the support. The pretreated support was collected by vacuum filtration, washed with isopropyl alcohol to remove reaction by-products, and air-dried. Mass of the pretreated product showed the desired sub-monolayer coverage by DETA silane was achieved.

Example 2

Deposition of Polyfunctional Oligomeric Polymer

See (Step 104), FIG. 2b

A solution containing 18.0 mL of polyethyleneimine (PEI) (423 g/mole; 1.07 g/mL; 45.5 mmole) in 100 mL of diglyme was prepared. 11.4 mL of 3-isocyanatopropyltrimethoxysilane was added to the solution and stirred overnight at ambient temperature to form PEI silane. The pretreated support product obtained in Example 1 was mixed with 10 mL of PEI silane solution, representing a solution volume less than the total pore volume of the pretreated silica support sample. The pretreated silica support sample was mixed thoroughly by rotating and stirring the mixture to obtain a uniform distribution of PEI silane in the pores of the porous silica. Sample was placed in a thick-walled thermolysis tube sealed with a threaded teflon stopper and heated in an oven at $\sim 80^\circ \text{ C}$. for 18 hours to deposit and attach PEI silane at surfaces of pores of the silica support. Product was cooled to ambient temperature, washed with isopropyl alcohol to remove reaction by-products, and air-dried. The polymer deposition step can be repeated if additional polymer loading is desired. Mass of the product showed incorporation of PEI silane. BET surface area analysis revealed that the product still maintained high surface area and an open pore structure.

Example 3

Backfilling of Intermediate Treated Support

See {Step 106}, FIG. 2c

The DETA/PEI-coated silica product from Example 2 was suspended in 150 mL of toluene and treated with 4 mL of DETA silane, representing an excess quantity (above monolayer coverage) of DETA silane. DETA silane was added to the suspension and the mixture was heated at a (solvent) reflux temperature of 110° C . for 4 hours to produce the fully functionalized sorbent product. Sorbent product was collected by vacuum filtration, washed copiously with isopropyl alcohol and air-dried. Mass of the sorbent product showed that additional DETA coverage had been achieved in the product. Brunauer, Emmett, and Teller (BET) surface area

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analysis revealed that the sorbent product retains a high surface area and open pore structure.

Example 4

Sorption Capacity Tests of Sequentially Functionalized Sorbent

The sequentially functionalized sorbent was prepared in a 3-stage synthesis that included: 1) pretreatment with a 12.5% DETA pre-fill; 2) a one-time deposition with PEI, which number is not limited; and 3) backfilling with DETA silane. Sorption data were characterized using a gas stream containing 0.5% CO_2 in air. Baseline concentration of CO_2 prior to contact with the sorbent is shown in FIG. 3. At time $T=0$, the stream of air containing CO_2 was introduced through a bed containing the sorbent. Results showed a precipitous drop in CO_2 concentration to below a limit of detection for the NDIR measuring equipment. CO_2 levels equilibrated at $\sim 0.5\%$ following saturation (e.g., at times >40 minutes in the reported test). Sorbent results showed a CO_2 sorption capacity of $\sim 4.6\%$ by weight, with sorption kinetics greater than about 700 min^{-1} . Preliminary tests showed from 2 to 23 times better sorption kinetics and an approximately 2-fold better sorption capacity compared to an EDA-based silica sorbent used as a control. Results for the sequentially functionalized sorbent of the invention further achieved approximately 2.5 times lower residual concentrations of CO_2 (at equilibration) compared to a $\sim 30\%$ MEA liquid sorbent at comparable capacity.

We claim:

1. A sequentially functionalized sorbent for chemical capture and retention of a target analyte, comprising:

a porous support comprising pores functionalized with short-chain alkyl aminosilanes interspersed between polyfunctional oligomeric aminosilanes, wherein said short-chain alkyl aminosilanes include a tether group with a chain length of 4 atoms or less and a terminal amine group coupled thereto with a chain length of 7 atoms or less, wherein said short-chain alkyl aminosilanes and said oligomeric aminosilanes provide a uniform density of active binding sites within said pores defined by a quantity of nitrogen greater than or equal to about $5.0 \times 10^{-3} \text{ mmol N per m}^2$ of pore surface area for chemical binding and retention of said target analyte therein.

2. The sequentially functionalized sorbent of claim 1, wherein said short-chain alkyl aminosilanes are of a size below about 20 \AA and said polyfunctional oligomeric aminosilanes are of a size greater than about 20 \AA .

3. The sequentially functionalized sorbent of claim 1, wherein said short-chain alkyl aminosilanes are selected from the group consisting of: aminopropylsilanes; 3-(2-aminoethyl)aminopropylsilanes; 3-(diethylenetriamine)-propylsilanes; and combinations thereof.

4. The sequentially functionalized sorbent of claim 1, wherein said terminal amine group portion of said short-chain alkyl aminosilanes comprises 3-diethylenetriamine (DETA).

5. The sequentially functionalized sorbent of claim 1, wherein said short-chain alkyl amino silanes include 3-diethylenetriamine (DETA)-propyltrimethoxysilane.

6. The sequentially functionalized sorbent of claim 1, wherein said polyfunctional oligomeric alkyl aminosilanes include polyethyleneimine (PEI).

7. The sequentially functionalized sorbent of claim 1, wherein said binding sites further include a functional group selected from the group consisting of: thiols; carboxylates; sulfonates; phosphonates; phosphines; heteroaromatic